

Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides

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Abstract

A mix-valenced nickel oxide was obtained from nickel nitrate aqueous solution through a precipitation with sodium hydroxide and an oxidation by sodium hypochlorite. Furthermore, the oxide was heated under microwave-assisted to fabricate a high-active mix-valenced nickel oxide (assigned as NiO_x). Pure nickel oxide was obtained from the NiO_x by calcination at 300, 400 and 500 °C (labeled as C300, C400 and C500, respectively). They were characterized by thermogravimetry (TG), X-ray diffraction (XRD), infrared spectroscopy (IR), temperature-programmed reduction (TPR), nitrogen adsorption at 196 °C and scanning electron microscopy (SEM). Their catalytic activities towards the degradation of 4-chlorophenol were further studied under continuous bubbling of air through the liquid phase. Also, the effects of pH, temperature and kinds of nickel oxide on the efficiency of the microwave-enhanced catalytic degradation (MECD) of 4-chlorophenol have been investigated. The results showed that the 4-chlorophenol had degraded completely into harmless products (CO₂·H₂O and mineral acids) within 5 min of investigation, under pH 7 and *T* = 70 °C over the fabricated NiO_x.

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1. Introduction

Environmental pollution is a serious challenge for the whole world. Aromatic pollutants in industrial wastewater, in particular phenol and phenolic derivatives have been on the EPAs priority pollutants list since 1976 [1]. Phenolic compounds show low biodegradability. Some of the most toxic phenolic compounds are chlorinated phenols, which are widely used as intermediates in the synthesis of the higher chlorinated congeners, certain dyes and pesticides [2]. These compounds are considered hazardous pollutants because of their potential to harm human health. Indeed, it is necessary to eliminate them from industrial wastewater before it flows into streams. In recent years, many methods such as sonochemical degradation [3–5], photocatalytic degradation [6–10],

advanced oxidation process with UV/H₂O₂ (AOP) [11], catalytic oxidation [12], wet air oxidation [13] and microwave-enhanced advanced oxidation processes [14–18] have been used for efficient removal of phenolic compounds from wastewater. Using conventional techniques to eliminate these kinds of compounds may be difficult as they are usually present at low concentrations in water or they are especially refractory to the oxidants. Therefore, alternative effective processes for the abatement of such contaminants have to be explored. In previous work we have succeeded in developing microwave-enhanced catalytic degradation (MECD) [19] method on phenol that can degrade completely into harmless products within 8 min. We suggest that the MECD method is an efficient process for the treatment of phenolic compounds.

The heating effect of high-frequency fields on some materials was recognized even in the 19th century. The mechanism of energy transfer using a microwave field is very different from that of the three well-established modes of heat transfer, that is, conduction, radiation, and convection. During the last few decades, microwave irradiation technology has already been

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applied to industry, family, material science [20] and environmental organic pollution for polycyclic aromatic hydrocarbons (PAHs) [21–23], polychlorinated biphenyls (PCBs) [24], etc. Due to the properties of internal and volumetric heating (dipole rotation and/or ionic conduction), thermal gradients during microwave processing are avoided, providing a uniform environmental for reaction. Therefore, microwave heating has shown advantages over the conventional heating method in terms of energy efficiency, higher reaction rates and shortened reaction times [25]. The use of microwaves as a source of energy is rapidly becoming more economic and convenient.

Based on the previous work [19], using solid materials as catalysts are of great interest and important in purifying wastewaters containing phenol. Transition metal oxides have proved to be active in the catalytic reactions of the degradation of phenol and its derivatives [14,26,27]. Among them, the catalysts based on the oxides of nickel and cobalt appears to be especially efficient. In this work we study the activity of fabricated nickel oxides on the degradation of 4-chlorophenol by a MECD method.

2. Experimental

2.1. Preparation of nickel oxide

Under alkaline electrolyte solution, Chigane et al. [28] had succeeded to prepare hexagonal-type NiO_x thin films with potentiostatic electrodeposition. Also, Konoka et al. [29] and Nakagawa et al. [30] obtained nickel peroxide from nickel sulfate with sodium hypochlorite (NaOCl) in an alkaline solution. It is well known that NaOCl is an excellent oxidizing reagent for preparation of NiO_2 , which is a strong oxidant towards organic oxidation [31]. These properties give us the idea that the preparation and functionality of the high-valenced nickel oxide can be approached. A mix-valenced nickel oxide was synthesized by the precipitation–oxidation method in an aqueous solution. The process was carried out at 70 °C with dropwisely added 50 ml of 0.6 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to the 100 ml of 3.2 M NaOH solution to obtain as-prepared $\text{Ni}(\text{OH})_2$. Then, a 100 ml of NaOCl (12 wt.%) was introduced drop by drop under constant stirring to oxidize the $\text{Ni}(\text{OH})_2$. Furthermore, the obtained oxide was heated for 10 min in air in a microwave apparatus (100 W, 2450 MHz, CEM, USA). The precipitate was then filtered, washed with deionized distilled water and dried in an oven at 110 °C for 20 h. The dried product was ground and put in a desiccator as a fresh sample (marked as NiO_x). The NiO_x was calcined separately at 300, 400 and 500 °C for 3 h to obtain the pure nickel oxide (labeled as C300, C400 and C500, respectively).

2.2. Characterization of nickel oxide

Thermal gravimetric analysis (TG/DTG) was carried out using a Seiko SSC5000 TG system. The rate of heating was maintained at 10 °C min^{-1} and the mass of the sample was ~10 mg. The measurement was carried from room temperature to 700 °C under nitrogen flowing with a rate of 100 ml min^{-1} .

X-ray diffraction (XRD) measurements were performed using a MAC Science MXP18 diffractometer with $\text{Cu K}\alpha_1$

radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA with a scanning speed in 2θ of 4° min^{-1} . The crystallite sizes of nickel oxide were calculated using the Scherrer equation.

Nitrogen adsorption isotherms at –196 °C were performed volumetrically with Micromeritics ASAP 2010. The nickel oxides were pre-outgassed at 5×10^{-5} Torr for 3 h at 110 °C. The surface area was determined according to the adsorption isotherm.

Reduction behavior of nickel oxide was studied by temperature-programmed reduction (TPR). About 50 mg of the sample was heated in a flow of 10% H_2/N_2 atmosphere at a flow rate of 10 ml min^{-1} . During TPR experimental, the temperature was increased by 7 °C min^{-1} increment from room temperature to 600 °C.

The infrared spectra were obtained by a Nicolet 5700 FT-IR spectrometer in the range of 400–2000 cm^{-1} . One milligram of each powder sample was diluted with 200 mg of vacuum-dried IR-grade KBr and subjected to a pressure of 8 tonnes.

The surface morphologies of nickel oxide nanoparticles were observed by means of a scanning electron microscope (JSM-6330TF) operated at 10 kV.

2.3. Degradation of 4-chlorophenol

The MECD experiments for degradation of 4-chlorophenol (4-CP) were carried out in a thermostatic microwave apparatus (CEM, Discover, USA, 2450 MHz, 300 W, temperature was controlled with IR sensor) upon continuous stirring, likewise providing an equal level of all parameters describing the state of the system (temperature, pH, catalysts and initial concentration of 4-CP). A 60 ml of aqueous 4-CP solution (initial concentration of 200 ppm) was used for each experimental run. Air was bubbled in the solution for 30 min before adding the catalyst. Then, a fit amount of catalyst was suspended in the solution. The air was continuously bubbled during the runs. Concentrations of the residual 4-CP and products were determined by HPLC and UV–vis. The absorbance of 298 nm was used to measure the concentration of 4-CP.

The chromatographic experiments were performed using high-pressure liquid chromatograph Agilent 1100 Series equipped with diode array detector and a column oven. A 125 mm \times 4 mm reverse-phase C-18 column (chrompack) was used for separation. The injection volume was 20 μl , flow rate was 1.0 ml min^{-1} , UV detector wavelength was 270 nm and column oven temperature maintained 25 °C. The compounds were eluted with acetonitrile/water (50/50 (v/v)). Calibration graphs at five concentration levels were prepared from working solutions containing the 4-CP in the range 0.1–200 mg/l ($R^2 = 0.9997$, S.D. = 2.15).

3. Results and discussion

3.1. Characterization of the fabricated high-valence nickel oxide— NiO_x

Fig. 1 shows the TG/DTG curves of the NiO_x under a dynamic nitrogen (100 ml min^{-1}) environment. The TG curve

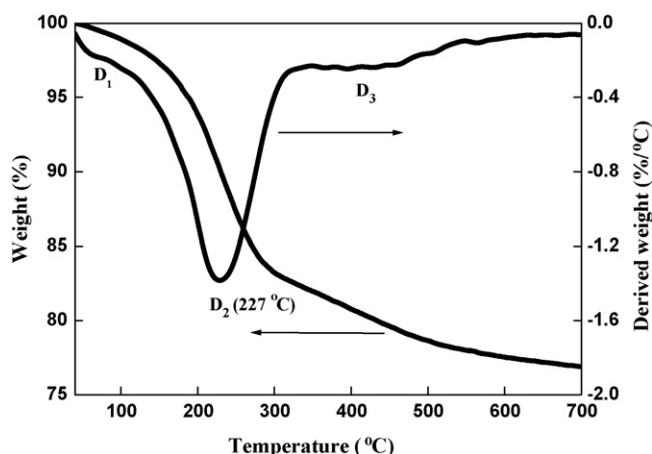


Fig. 1. TG/DTG profiles of the fabricated NiO_x in a dynamic nitrogen environment.

shows three weight loss steps (assigned as D_1 , D_2 and D_3) and the DTG curve shows the maximum loss rate of a D_2 step at 227 °C, while both the D_1 and D_3 steps are not obvious. Prior to 100 °C, the rapid weight loss should be from desorption of water on NiO_x surface in heating process. The weight loss of 12% in D_2 step is mainly caused by the decomposition of an unstable NiO_x that transfers into NiO according to Eq. (1):

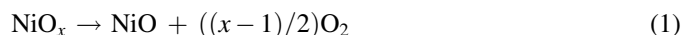


Fig. 2 shows the TPR profile of both the fabricated NiO_x and commercial NiO_2 . The reductive signals (labeled as R_1 and R_2) of NiO_x indicate two consecutive steps at 176 and 351 °C (see Fig. 2(a)). Mile et al. [32] found the same tendency of reduction on Ni/SiO_2 catalyst and suggested the species was Ni_2O_3 . Nakagawa et al. [30] prepared the NiO_2 (nickel peroxide) with the NaOCl oxidizing agent. Fig. 2(b) also shows the R_1 and R_2 signals around 157 and 304 °C for the commercial NiO_2 (Aldrich). Further reveals that the peaks of NiO_x can be assigned to the reduction of NiO_2 and NiO species for R_1 and R_2 , respectively. The NiO_2 is initially reduced to NiO , then,

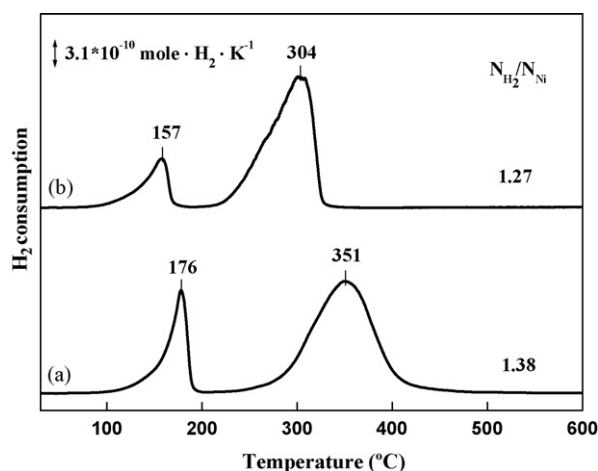


Fig. 2. TPR profiles of: (a) NiO_x and (b) commercial NiO_2 .

subsequently reduced to Ni according to Eqs. (2) and (3):



The content of oxygen for each nickel oxide species in NiO_x is quantitatively determined from the consumption of hydrogen in TPR traces. The relative area of R_1 and R_2 ($N_{\text{H}_2}/N_{\text{Ni}}$ ratio) are 0.38 and 1.0 for NiO_x . The relative area of R_1 and R_2 are 0.27 and 1.0 for commercial NiO_2 . Comparison with the theoretical values (1 and 1, respectively) showed that based on Eqs. (2) and (3), we prove that the stoichiometric of x in NiO_x is 1.38, while only 1.27 for the commercial NiO_2 . Therefore, the fabricated NiO_x is confirmed to be a high-valence nickel oxide with a non-stoichiometric chemical formula of $(\text{NiO})_{0.6}(\text{NiO}_2)_{0.4}$. The content of Ni^{4+} may be the factor to affect the activity for the degradation of 4-chlorophenol.

3.2. Characterization of nickel oxide

In order to obtain pure nickel oxide, the fabricated NiO_x is calcined separately under 300, 400 and 500 °C to obtain the pure nickel oxide (labeled as C300, C400 and C500, respectively).

Fig. 3 presents the XRD patterns of the NiO_x and the refined nickel oxides (C300, C400 and C500). The faint diffraction peaks at ca. 19.0° and 38.4° for the NiO_x (Fig. 3(a)) reveals that the fine particle size is similar to the β - NiOOH with the diffraction peaks at (0 0 1) and (1 0 0) planes. All samples except NiO_x show the cubic crystal structure (Fig. 3(b)–(d)), with three peaks at ca. 37.2°, 43.2° and 62.8°, corresponding to (1 1 1), (2 0 0) and (2 2 0) planes for NiO , respectively. The XRD pattern indicates that there is no impurity for the C300, C400 and C500 samples. According to the diffraction patterns and the width of the (2 0 0) diffraction pattern of NiO crystalline, the calculated particle size grows from 5.2 to 16.6 nm (given in the third column of Table 1) with the calcined temperature (T_C). The higher the T_C , the sharper the diffraction peaks, indicating the degree of crystalline is progressive growth with temperature.

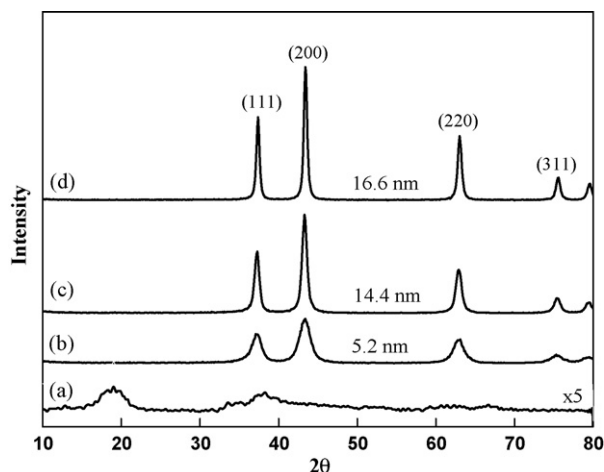


Fig. 3. XRD patterns of nickel oxides: (a) NiO_x ; (b) C300; (c) C400; (d) C500.

Table 1
Characterization and rate constant of the 4-CP degradation over nickel oxides

Catalyst	XRD		S_{BET} (m ² /g)	TPR		Degradation of 4-CP	
	Structure	d (nm)		T_{red} (°C)	$N_{\text{H}_2}/N_{\text{Ni}}$	α_{25} (%) ^a	k (min ^{−1})
NiO _x	–	–	211	176, 351	1.38	100	0.146
C300	Cubic	5.2	139	306, 356	1.10	42	0.013
C400	Cubic	14.4	89	334, 370	1.13	26	0.008
C500	Cubic	16.6	33	334, 378	1.13	26	0.008

^a Degree of phenol conversion is determined at 25 min.

The IR spectra of the NiO_x and the refined nickel oxides (C300, C400 and C500) are shown in Fig. 4. The broad absorption bands centered around 3430 and 1630 cm^{−1} are assigned to the existence of water, the absorption bands around 1530–1320 cm^{−1} indicate the existence of carbonate for all samples. The appearance of 570 cm^{−1} absorption band (Fig. 4(a)) indicates that only the fabricated NiO_x possesses in-plane vibration of hydrogen-bonded hydroxyl group. Whereas, the absorption band of 570 cm^{−1} disappears for the refined nickel oxides (Fig. 4(b)–(d)). Combined with the analysis of XRD, we can further confirm that the purity of nickel oxide.

Fig. 5 displays the TPR profiles of the refined nickel oxides (C300, C400 and C500). All samples show a similar TPR profile with two overlapped peaks. It means that different particles size distributes in the refined nickel oxides. A qualitative analysis of the TPR profile shows that the reduction peak (T_{red}) shifts to higher temperatures as the T_{C} increases (as can be seen in Fig. 5 and the fifth column of Table 1), i.e., the T_{red} of C300 sample is 306 and 356 °C. While, the T_{red} of C500 sample shifts to 334 and 378 °C. Also, the ratio of nickel oxide species for the calcined products is quantitatively determined from the consumption of hydrogen in TPR traces (list in the sixth column of Table 1). All the $N_{\text{H}_2}/N_{\text{Ni}}$ ratio is approached 1.0 that reveals the reductive behavior of NiO.

The surface area (S_{BET} , m² g^{−1}) of nickel oxides is determined with nitrogen adsorption isotherms measured at −196 °C. The data of S_{BET} are given in the fourth column of

Table 1. The results show that the increase of T_{C} induces a decrease in its surface area (i.e., C500 < C400 < C300 < NiO_x). The induced decrease due to the thermal treatment might be attributed to the grain growth of particles or collapse of pores. These phenomena can be shown in the SEM images. Fig. 6 presents the SEM images of the NiO_x and the refined nickel oxides (C300, C400 and C500). There are many different pores in the nanosolids. Some of them are connected to each other and some isolated. The pore shape is irregular and the pore size is not uniform. It is obvious that the increase of T_{C} induces an increase in its channel, i.e., NiO_x (pore size approaches 5.2 nm) < C300 (7.0 nm) < C400 (13.5 nm) < C500 (26.9 nm). The particles size increases with the calcined temperature too.

3.3. Degradation of 4-chlorophenol over nickel oxides

Concentrations of the residual 4-CP and products during the MECD process are illustrated by UV–vis and HPLC. Fig. 7 shows the representative UV–vis spectra of 4-CP degraded during MECD process over the NiO_x under pH 7 and $T = 70$ °C. The absorbance of 4-CP (found at 298 nm) and some intermediate compounds (new absorption bands found at 225, 248 and 284 nm) are distinguished. All the absorption bands are disappeared with the degradation time. The trends show that the 4-CP is degraded completely within 5 min over the fabricated NiO_x. In order to understand whether the content of Ni⁴⁺ over the fabricated NiO_x can promote the activity for the

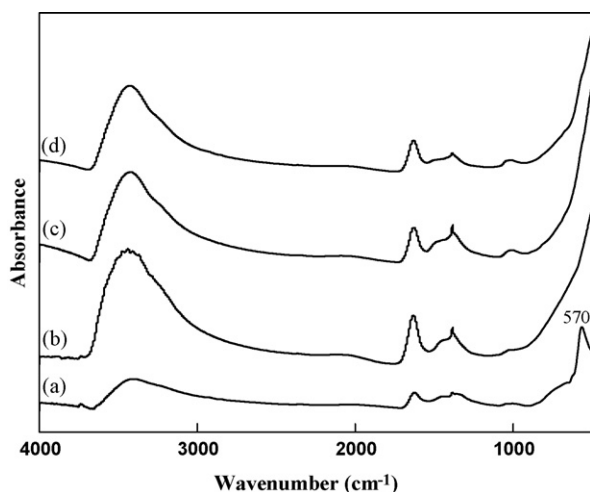


Fig. 4. IR spectra of nickel oxides: (a) NiO_x; (b) C300; (c) C400; (d) C500.

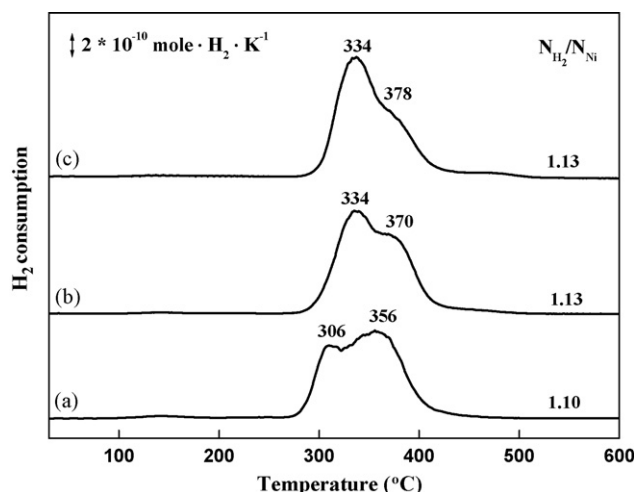


Fig. 5. TPR profiles of nickel oxides: (a) C300; (b) C400; (c) C500.

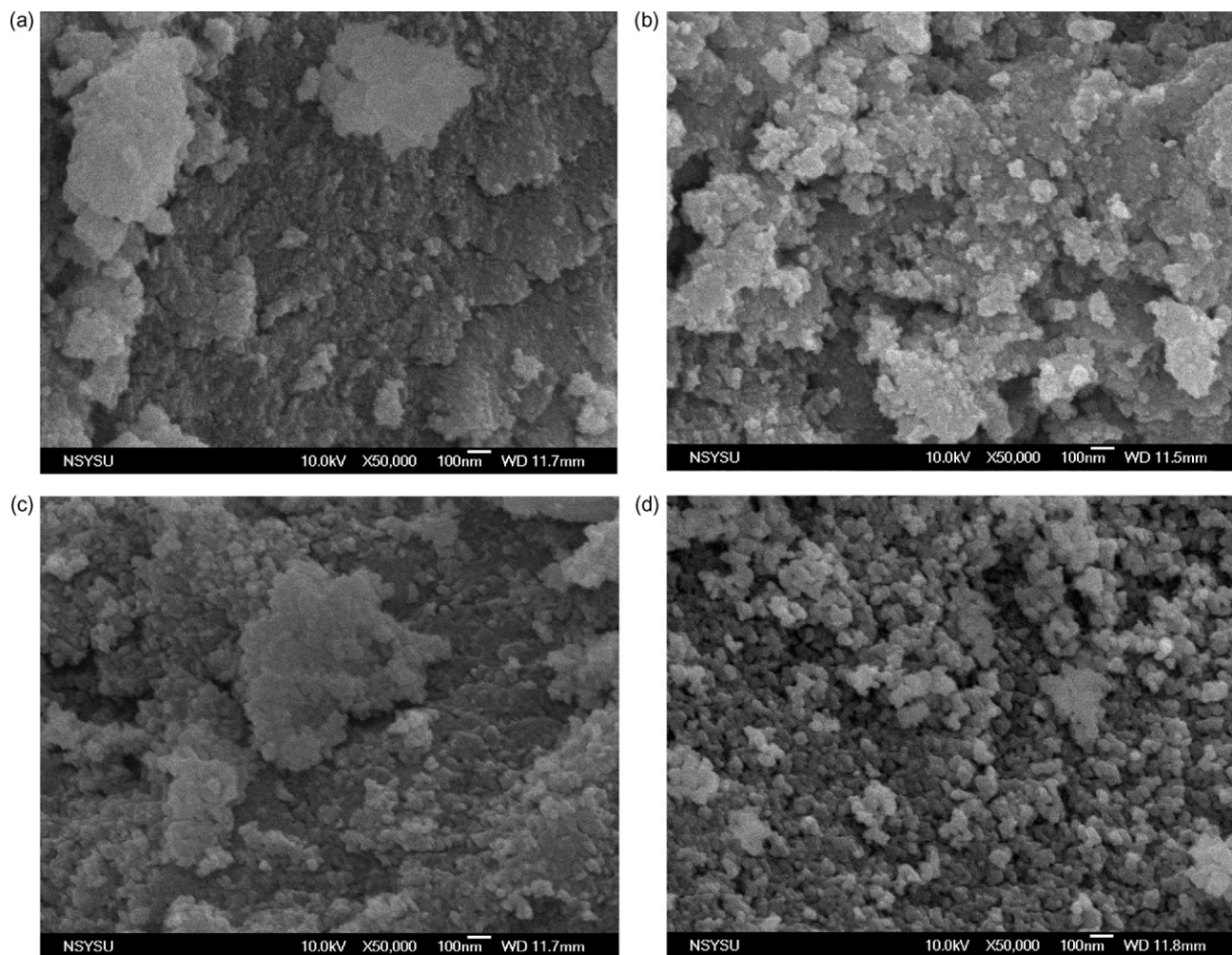


Fig. 6. SEM images of nickel oxides: (a) NiO_x ; (b) C300; (c) C400; (d) C500.

degradation of 4-chlorophenol, the analysis of TPR for used catalyst are proceeding. Comparison the TPR of fresh (Fig. 2(a)) with used (Fig. 8) NiO_x catalyst, shift of T_{red} for R_1 and R_2 accompanied with the decreasing of R_1 area further

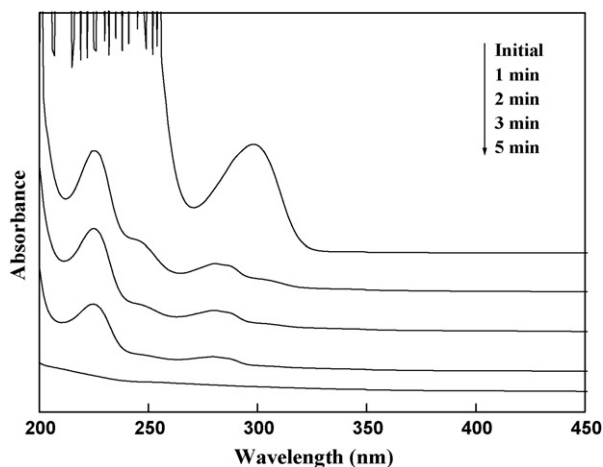


Fig. 7. UV-vis spectra of 4-CP degraded during MECD method over fabricated NiO_x under pH 7 and $T = 70^\circ\text{C}$.

suggests that the surface oxygen on high-valence state NiO_x participates and promotes the catalytic oxidation of 4-CP.

In order to trap the intermediates, the HPLC has been advanced. Fig. 9 shows the HPLC spectra of 4-CP degraded during MECD over the NiO_x under pH 7 and $T = 70^\circ\text{C}$. The peak appears at 2.5 min which is the species of 4-CP. This peak

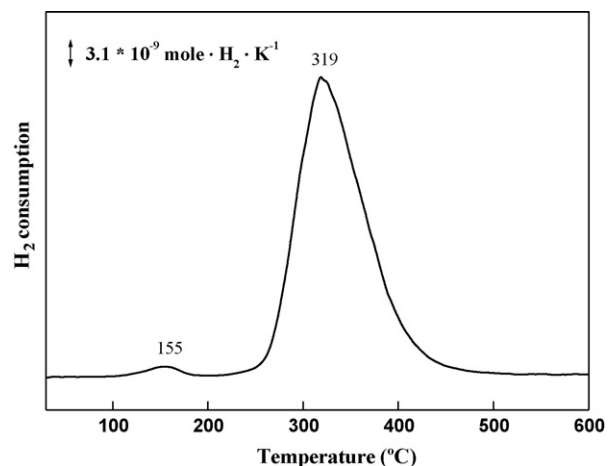


Fig. 8. TPR profile of the fabricated NiO_x after degradation of 4-CP.

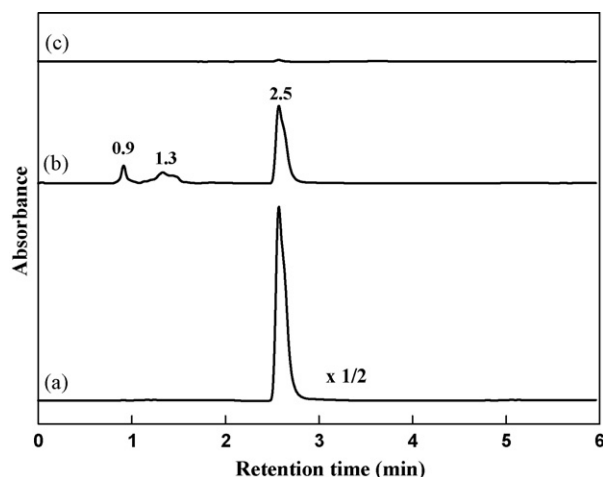


Fig. 9. HPLC spectra of 4-CP degraded during MECD method over fabricated NiO_x under pH 7 and $T = 70^\circ\text{C}$: (a) initial; (b) 30 s; (c) 5 min.

gradually diminishes with the proceeding of the MECD. In the same time, other small peaks appear at 0.9 and 1.3 min that is found to be the intermediates after 30 s degradation (Fig. 9(b)) and disappears after complete degradation (Fig. 9(c)). We suggest that the 4-CP is degraded completely into harmless products (CO_2 - H_2O and mineral acids).

Figs. 10–12 show catalytic activities of MECD for 4-CP over nickel oxides. The tendency of degradation is consistent with the results reported by Christoskova et al. [33]. They found that the complete degradation of 4-CP is achieved after 20 min under 35°C and pH 6 with Ni-oxide. Another complete degradation with the Fenton system is achieved after 40 min at 25°C [2]. Excitingly, in our results show that the complete degradation of 4-CP only needs 5 min. We think that under the irradiation of microwave, the electrophilic oxygen ions (O_2^- , O^- and O^{2-}) are easy donated to participate the degradation of 4-CP via the coupling effect between microwave and active oxygen species on high-valenced nickel oxide surface. Fig. 10 demonstrates the 4-CP can be totally eliminated in the pH ranges of 4–10 within 5 min by the MECD method over fabricated NiO_x catalyst under 70°C . Obviously, the fastest rate

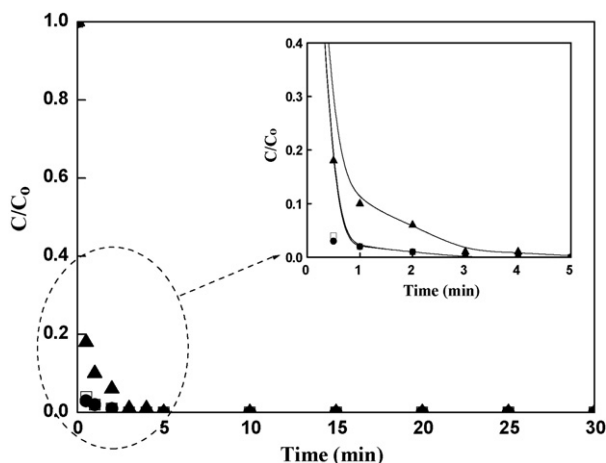


Fig. 10. The effect of the pH on the degradation of 4-CP by MECD method over fabricated NiO_x under 70°C : (□) pH 4; (●) pH 7; (▲) pH 10.

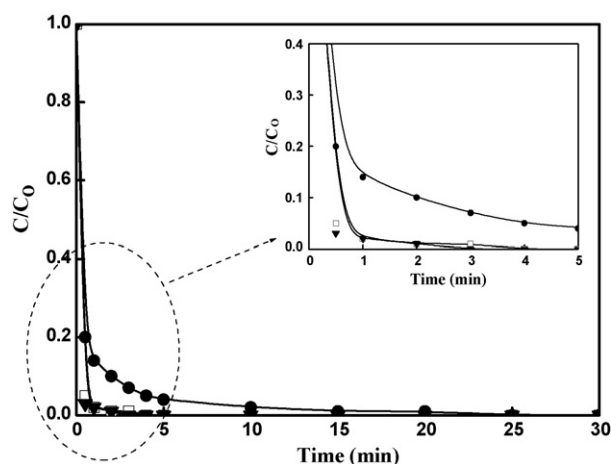


Fig. 11. The effect of the temperature on the degradation of 4-CP by MECD method over fabricated NiO_x under pH 7: (●) 40°C ; (□) 55°C ; (▼) 70°C .

of 4-CP degraded occurred within 30 s (the degree of conversion can attain 80%) under different pH ranges. Compare this result with Hao et al. [34], who use the pulsed discharge as active species, enhance degradation induced Fenton-like reactions must have a long induction period. We affirm that the MECD method is a promising novel technology for the removal of organic contaminants (i.e., phenol [19], 4-CP). The microwave irradiation induces a rotation and a migration violently for the motion of polar molecules, resulting in a fast increase of the solution temperature due to friction. Also, the violent motion of polar substances can lead the molecules to a higher excited state through an increase of collision numbers between reactants, resulting in accelerating the rate of 4-CP degraded. It means that the simultaneous combination of microwave and catalysis can effectively degrade several kinds of intermediates produced in the course of 4-CP degradation, eventually driving the intermediates into CO_2 - H_2O and mineral acids. A complete degradation is achieved within 5 min under pH ranges of 4–10 and 70°C .

The effect of temperature on the activity by MECD method over fabricated NiO_x catalyst is investigated in the temperature

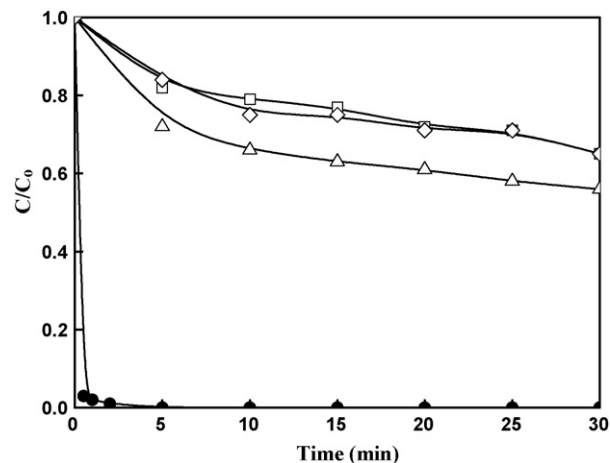


Fig. 12. Comparison of the degradation of 4-CP by MECD method over nickel oxides under pH 7 and $T = 70^\circ\text{C}$: (●) NiO_x ; (△) C300; (□) C400; (◇) C500.

ranges from 40 to 70 °C under pH 7. Fig. 11 shows that the fastest rate of 4-CP degraded also occur within 30 s under these temperature ranges. A complete degradation is achieved within 20, 4 and 3 min under 40, 55 and 70 °C, respectively. The result is identical with Christoskova et al. [35,36], Akyurtlu et al. [14] and Liou et al. [37]. They also found that the degradation of 4-CP without microwave irradiate is dependant on the temperature.

Fig. 12 compares the degradation of 4-CP by MECD method over fabricated NiO_x and refined nickel oxides under 70 °C and pH 7. The degradation of 4-CP over each sample generally increases with the reaction time. Clearly, the activity of fabricated NiO_x is better than other nickel oxides. Within 5 min, the 4-CP can be degraded completely over fabricated NiO_x . However, even within 30 min, the 4-CP only approached 40% degradation over refined nickel oxides (C300, C400 and C500). To compare the relative activity of the catalysts, kinetic parameters of the degree of conversion (α_{25} , determined at the 20 min) and rate constant (k) are listed in the seventh and last columns of Table 1. The rate constant on NiO_x catalyst is two orders of magnitude higher than that on C300, C400 and C500 samples.

Based on the characterization of catalysts, the driving force for NiO_x may be attributed to the high-valence state and surface area. According to the TPR results (Fig. 2), the lower temperature reduction (R_1) reveals that the bond strength of Ni–O on NiO_x is weak and provides easily active oxygen to oxidize the 4-CP. Compared to the S_{BET} (the fourth column of Table 1) of nickel oxides, the activity increases significantly by increasing the S_{BET} , i.e., fabricated NiO_x ($S_{\text{BET}} = 211 \text{ m}^2 \text{ g}^{-1}$) > C300 ($S_{\text{BET}} = 139 \text{ m}^2 \text{ g}^{-1}$) > C400 ($S_{\text{BET}} = 89 \text{ m}^2 \text{ g}^{-1}$) > C500 ($S_{\text{BET}} = 33 \text{ m}^2 \text{ g}^{-1}$). Apparently, the relative activity affected significantly with the oxidation state of nickel and surface area of nickel oxide.

4. Conclusion

A novel and environmentally friendly process for the degradation of 4-CP is developed. From the exciting results of the present work, the conclusions have been made as follows:

- (1) The fabricated NiO_x is confirmed to be a high-valence nickel oxide with a non-stoichiometric chemical formula of $(\text{NiO})_{0.6}(\text{NiO}_2)_{0.4}$. Pure nickel oxide can be refined by calcinations of NiO_x above 300 °C.
- (2) 4-CP is degraded completely into harmless products (CO_2 - H_2O and mineral acids) by MECD method within 5 min under pH 7 and $T = 70$ °C over fabricated NiO_x .
- (3) Activity of 4-CP degraded is strongly dependent on the oxidation state of nickel and surface area of nickel oxide, i.e., NiO_x ($>+2$ and $S_{\text{BET}} = 211 \text{ m}^2/\text{g}$) \gg C300 ($+2$ and $S_{\text{BET}} = 139 \text{ m}^2/\text{g}$) > C400 ($+2$ and $S_{\text{BET}} = 89 \text{ m}^2/\text{g}$) > C500 ($+2$ and $S_{\text{BET}} = 33 \text{ m}^2/\text{g}$).

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